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Spectroscopy measurements for determination of polymer particle size distribution

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ABSTRACT

Polymer and copolymer emulsion lattices based on styrene and butyl-metacrylate monomers are commercially important for many paints, adhesives, and coatings applications. The latex properties depend strongly on the copolymer composition, and particle size distribution, which in turn is function of the preparation of the latex and on the formulation of the emulsion designed for the particular application. This paper describes the implementation of multiwavelength spectroscopy measurements for size and distribution of the latex emulsions. The quantitative interpretation of the transmission spectrum is performed in the portion where no absorption is present (300–820 nm) leading to reliable estimated of particle size populations in the range of 0.02–20 μm . Particle size and particle size distribution of polymers and copolymers as function of reaction time and emulsion formulation are found in agreement with Smith Ewart (case 2 kinetics). The possibility of obtaining information from a single multiwavelength measurement makes UV–Vis spectroscopy a powerful tool for characterization of dispersed systems.

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1. Introduction

Emulsion polymerization is a free radical polymerization in a heterogeneous system and it is a process of considerable industrial importance used in the manufacture of a wide range of products including paints, toners, adhesives, coatings, and other synthetic materials. It has applications in bioseparations through the functionalization of latex particles and offers great promise for the synthesis of nanomaterials [1]. During batch emulsion polymerization of sparsely water-soluble monomers such as styrene, three different time-separated intervals can be distinguished: the interval I of the emulsion polymerization reaction is characterized by the disappearance of micelles and formation of particles (or particle nucleation). The interval II is characterized by the growth of the particles and the presence of monomer droplets, while the

interval III is characterized by the disappearance of the monomer droplets [2,3]. Nucleation of particles is assumed to take place mainly in the micelles when the emulsifier concentration of the initial emulsion exceeds the critical micellar concentration (CMC), which is named micellar nucleation. This mechanism considers that the majority of particles are formed from the population of monomer-swollen surfactant micelles. The rate of particle nucleation is directly proportional to the micellar concentration and to the rate of capture of radicals by the micelles; which is function of the diffusivity of the oligomeric radicals [3–5]. Particle size and particle size distribution (PSD) of the particles can provide information about the kinetics of polymerization, particularly concerning particle growth [6–8] and the nucleation mechanism [9–12], and strongly affect the latex properties [13]. Inferences on the nucleation mechanism from early-time particle size distribution data are not reliable because the time constant for particle nucleation is much smaller than the time constant for sampling the PSD. For instance, it has been shown that most of the information inferred from early-time PSD obtained from the experiments [10] is unreliable because of the stochastic broadening of the PSD that occurs after nucleation stops [14]. There are several techniques for the measurements of the particle size and the particle size distribution of the particles: transmission electron microscopy, in which all the sizes are treated with the same statistical weight [15] and extensive sample preparation (i.e. vacuum evaporation) are required,

Abbreviations: Au, absorbance units; UV–Vis, ultraviolet–visible; CMC, critical micellar concentration; PSD, particle size distribution.

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